

WHAT IS CLAIMED IS:

1. A process for the manufacture of a haloalkane comprising the steps of:
 - a) contacting carbon tetrachloride with an olefin in a reactor in the presence of a substantially dissolved catalytic copper compound and an organonitrile co-catalyst, wherein the co-catalyst is selected to be capable of distilling at a lower temperature than the desired haloalkane product, under conditions effective to produce a reaction mixture that contains a haloalkane adduct of carbon tetrachloride with the olefin,
 - b) distilling the reaction mixture in a catalyst recovery unit to produce an overhead stream or overhead streams containing unconverted reactants and recovered organonitrile co-catalyst and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in the desired haloalkane product,
 - c) separating the precipitated copper catalyst components of step b) from the fluid that is enriched in the desired haloalkane product and purifying by distillation the fluid to yield purified haloalkane product,
 - d) dissolving the precipitated copper catalyst components of step c) in the recovered organonitrile co-catalyst of step b) to produce a

solution of copper catalyst in a liquid containing the organonitrile co-catalyst and

- e) returning a portion of the copper catalyst solution in organonitrile co-catalyst from step d) to the reactor.

- 5 2. The process of claim 1 wherein the olefin is ethene and the desired haloalkane is 1,1,1,3-tetrachloropropane or the olefin is vinyl chloride and the haloalkane is 1,1,1,3,3-pentachloropropane, or the olefin is 1,1-dichloroethene and the haloalkane is 1,1,1,3,3,3-hexachloropropane, or the olefin is 2-chloropropene and the haloalkane product is 1,1,1,3,3-pentachlorobutane.
- 10
3. The process of claim 1 wherein the organonitrile co-catalyst is acetonitrile, propanenitrile, butanenitrile, 2-methylpropanenitrile, pentanenitrile, or 3-methoxypropanenitrile.
4. The process of claim 1 wherein the copper catalyst components which are present in an undetermined form during reaction are originally added to the system in the form of copper(I) chloride, which is the catalyst precursor.
- 15
5. The process of claim 1 wherein a portion of the unconverted reactants from step b) is returned to the reactor.
6. A process for the manufacture of 1,1,1,3-tetrachloropropane comprising the steps of:
- 20

- a) contacting carbon tetrachloride with ethene in a reactor in the presence of substantially dissolved copper catalyst components, wherein the copper catalyst components were originally added to the process in the form of cuprous chloride, and n-butyronitrile co-catalyst, under conditions effective to produce a reaction mixture that contains 1,1,1,3-tetrachloropropane, wherein the reactor preferably operates at 100-180° C and at 80-400 psig, with liquid residence time of 0.2-200 hours, and with liquid n-butyronitrile concentration from 10-50 wt%,
- b) distilling the reaction mixture in a catalyst recovery unit to produce an overhead stream or overhead streams containing unconverted reactants and recovered co-catalyst, and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in 1,1,1,3-tetrachloropropane, wherein the distillation is preferably done at a temperature of from 30-160° C, and at pressure 5-840 torr,
- c) separating the precipitated copper catalyst components from the bottoms slurry from b) and purifying the liquid by conventional means, such as distillation, to yield purified 1,1,1,3-tetrachloropropane,

- d) dissolving the precipitated copper catalyst components from c) in the recovered n-butyronitrile co-catalyst from b) to produce a solution of copper catalyst components in a liquid containing the co-catalyst and
- e) returning a portion of the catalyst solution from d) to the reactor.

- 5 7. The process for manufacture of 1,1,1,3-tetrachloropropane of claim 6 wherein in step a) the reactor operates at 120-160° C and at 100-300 psig, with liquid residence time of 1-50 hours, with the liquid n-butyronitrile concentration of 20-40 wt%, and in step b) the distillation is done at a temperature of from 88-112° C and at a pressure of 85-204 torr.
- 10 8. The process for manufacture of claim 7 wherein the reactor operates at 138° C and at 250 psig, with a liquid residence time of about 5 hours if a batch reaction is employed or 11 hours if a continuous reaction is employed, and with the liquid n-butyronitrile concentration of about 30 wt% and in step b) the distillation being done at a temperature of about 104° C and at a pressure
- 15 of 154 torr.
9. A process for the manufacture of a haloalkane comprising the steps of:
- a) contacting carbon tetrachloride with an olefin in a reactor in the presence of a substantially dissolved catalytic copper compound and an organonitrile co-catalyst, wherein the co-catalyst is selected to be
- 20 capable of distilling at a lower temperature than the desired

haloalkane product, under conditions effective to produce a continuous reactor effluent stream that contains a haloalkane adduct of carbon tetrachloride with the olefin,

- 5 b) continuously distilling the reactor effluent stream in a catalyst recovery unit to produce an overhead stream or overhead streams containing unconverted reactants and recovered co-catalyst and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in the desired haloalkane product,
- 10 c) separating the solid copper catalyst components of step b) from the fluid in a solids/liquid separation unit to produce a continuous, substantially liquid stream containing the desired haloalkane product and a solid product that contains the solid copper catalyst components or a slurry enriched in the solid catalyst components,
- 15 d) purifying by distillation the liquid stream containing the desired haloalkane product from step c) to produce a purified haloalkane product,
- 20 e) dissolving the solid copper catalyst components from step c) in the recovered co-catalyst stream from step b) to produce a solution of copper catalyst components in a liquid containing the co-catalyst and

f) continuously feeding a portion of the liquid catalyst/co-catalyst solution from step e) into the reactor.

10. The process of claim 9 wherein the olefin is ethene and the desired haloalkane is 1,1,1,3-tetrachloropropane or the olefin is vinyl chloride and the haloalkane is 1,1,1,3,3-pentachloropropane, or the olefin is 1,1-dichloroethene and the haloalkane is 1,1,1,3,3,3-hexachloropropane, or the olefin is 2-chloropropene and the haloalkane product is 1,1,1,3,3-pentachlorobutane.
11. The process of claim 9 wherein the organonitrile co-catalyst is acetonitrile, propanenitrile, butanenitrile, 2-methylpropanenitrile, pentanenitrile, or 3-methoxypropanenitrile.
12. The process of claim 9 wherein the copper catalyst components are originally added to the system in the form of copper(I) chloride, which is the catalyst precursor.
13. The process of claim 9 wherein a portion of the unconverted reactants from step b) is returned to the reactor.
14. The process of claim 9 wherein the catalyst recovery unit comprises a distillation column located above a hydrocyclone unit wherein the solids formed during distillation are continuously swept from the hydrocyclone using a liquid stream taken from the solids/liquid separation unit of step c).

15. A process for manufacture of 1,1,1,3-tetrachloropropane comprising the steps of:
- a) contacting carbon tetrachloride with ethene in a reactor in the presence of substantially dissolved cuprous chloride catalyst and n-butyronitrile cocatalyst, under conditions effective to produce a continuous reactor effluent stream that contains 1,1,1,3-tetrachloropropane, wherein the reactor operates at 100-180° C and at 80-400 psig, with liquid residence time 0.2-200 hours, and with liquid n-butyronitrile concentration from 10-50 wt%,
 - b) continuously distilling the reactor effluent stream in a catalyst recovery unit to produce an overhead stream or overhead streams containing unconverted reactants and recovered cocatalyst and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in 1,1,1,3-tetrachloropropane product, wherein the distillation is done at a temperature from 30-160° C, and at pressure of 5-840 torr,
 - c) separating the solid copper catalyst components from the fluid in a solids/liquid separation unit to produce a continuous, substantially liquid stream containing 1,1,1,3-tetrachloropropane product and either a substantially solid product that contains the solid copper catalyst components or a slurry that is enriched in the solid catalyst

components, wherein the solids/liquid separation device is a filter, a centrifuge or a hydrocyclone, and is preferably a hydrocyclone,

d) purifying by distillation the substantially liquid stream containing 1,1,1,3-tetrachloropropane product from c) to produce a purified 1,1,1,3-tetrachloropropane product,

e) dissolving the solid copper catalyst components from c) in the recovered n-butyronitrile co-catalyst stream from b) to produce a solution of copper catalyst components in a liquid containing the co-catalyst, and

f) continuously feeding a portion of a liquid catalyst/co-catalyst solution from e) into the reactor.

16. The process for the manufacture of 1,1,1,3-tetrachloropropane of claim 15 wherein in step a) the reactor operates at 120-160° C and at 100-300 psig with liquid residence time of 1-50 hours and with a liquid n-butyronitrile concentration of 20-40 wt% and in step b) the distillation is done at a temperature of 88-112° C and at a pressure of 85-204 torr.

17. The process for the manufacture of 1,1,1,3-tetrachloropropane of claim 16 wherein in step a) the reactor operates at a temperature of 138° C and at a pressure of 250 psig with liquid residence time of about 11 hours and with a

liquid n-butyronitrile concentration of 30 wt% and in step b) the distillation is done at a temperature of 104° C and at a pressure of 154 torr.

18. A process for the manufacture of a haloalkane comprising the steps of:

5 a) contacting carbon tetrachloride with an olefin in a reactor in the presence of a substantially dissolved catalytic copper compound and an organonitrile co-catalyst, wherein the co-catalyst is selected to be capable of distilling at a lower temperature than the desired haloalkane product, under conditions effective to produce a continuous reactor effluent stream that contains a haloalkane adduct of carbon tetrachloride with the olefin,

10 b) continuously distilling the reactor effluent stream in a catalyst recovery unit to produce an overhead stream containing unconverted reactants, recovered co-catalyst, and the desired haloalkane product, and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in the desired haloalkane product,

15 c) continuously distilling the overhead stream from b) to produce streams that are enriched in unconverted reactants and co-catalyst, respectively, and optionally also to produce a stream that is enriched in the desired haloalkane product,

20

- d) separating the solid copper catalyst components from the bottom fluid of step b) in a solids/liquid separation unit to produce a continuous, substantially liquid stream containing the desired haloalkane product and a solid product that contains the copper catalyst components or a slurry that is enriched in the solid catalyst components,
- e) optionally combining the stream that is enriched in the desired haloalkane product from step c) with the liquid haloalkane stream from step d),
- f) purifying by distillation the liquid stream containing the desired haloalkane product from d) or e) to produce a purified haloalkane product,
- g) dissolving the solid copper catalyst components from d) in the enriched co-catalyst stream from c) to produce a solution of copper catalyst components in a liquid containing the co-catalyst, and
- h) continuously feeding a portion of the liquid catalyst/co-catalyst solution from g) into the reactor.

19. The process of claim 18 wherein the olefin is ethene and the desired haloalkane is 1,1,1,3-tetrachloropropane or the olefin is vinyl chloride and the haloalkane is 1,1,1,3,3-pentachloropropane, or the olefin is 1,1-dichloro-

ethene and the haloalkane is 1,1,1,3,3,3-hexachloropropane, or the olefin is 2-chloropropene and the haloalkane product is 1,1,1,3,3-pentachlorobutane.

20. The process of claim 18 wherein the organonitrile co-catalyst is acetonitrile, propanenitrile, butanenitrile, 2-methylpropanenitrile, pentanenitrile, or 3-methoxypropanenitrile.
21. The process of claims 18 wherein the copper catalyst components are present in an undetermined form, but may be originally added to the system in the form of copper(I) chloride, which is the catalyst precursor.
22. The process of claim 18 wherein the unconverted reactants from step c) are returned to the reactor.
23. The process of claim 18 wherein the catalyst recovery unit comprises a distillation column located above a hydrocyclone unit wherein the solids formed during distillation are continuously swept from the hydrocyclone using a liquid stream taken from the solids/liquid separation unit of step d).
24. A process for the manufacture of 1,1,1,3-tetrachloropropane comprising the steps of:
- a) contacting carbon tetrachloride with ethene in a reactor in the presence of substantially dissolved cuprous chloride catalyst and n-butyronitrile co-catalyst, under conditions effective to produce a continuous reactor effluent stream that contains 1,1,1,3-

tetrachloropropane, wherein the reactor operates at 100-180° C and at 80-400 psig with liquid residence time 0.2-200 hours, and with liquid n-butyronitrile concentration from 10-50 wt%,

- 5 b) continuously distilling the reactor effluent stream in a catalyst recovery unit to produce an overhead stream containing unconverted reactants and recovered co-catalyst and less than five percent of the 1,1,1,3-tetrachloropropane contained in the reactor effluent, and a bottoms stream comprising a slurry of precipitated copper catalyst components in a fluid that is enriched in 1,1,1,3-tetrachloropropane product, wherein the distillation is done at a temperature of from 30-10 160° C, and at pressure 5-840 torr,
- c) continuously distilling the overhead stream from b) to produce streams that are enriched in unconverted reactants and co-catalyst, respectively, wherein the co-catalyst stream contains less than 15 percent of the 1,1,1,3-tetrachloropropane contained in the reactor effluent stream, and
- d) separating the solid copper catalyst components from the bottom fluid of step b) in a solids/liquid separation unit to produce a continuous, substantially liquid stream containing greater than 80% 20 of the 1,1,1,3-tetrachloropropane that is contained in the reactor effluent, and either a solid product that contains the copper catalyst

components or a slurry that is enriched in the solid catalyst components, wherein the solids/liquid separation device is a filter or a centrifuge or a hydrocyclone, and is preferably a hydrocyclone, and

e) distilling the liquid stream containing the 1,1,1,3-tetrachloropropane product from d) to produce a purified 1,1,1,3-tetrachloropropane product,

f) dissolving the solid copper catalyst components from d) in the enriched co-catalyst stream from c) to produce a solution of copper catalyst components in a liquid containing the co-catalyst, and

g) continuously feeding a portion of the liquid catalyst/co-catalyst solution from f) into the reactor.

25. The process for the manufacture of 1,1,1,3-tetrachloropropane of claim 24 wherein in step a) the reactor operates at 120-160° C and at 100-300 psig with a liquid residence time of 1-50 hours and with a liquid n-butyronitrile concentration of from 20-40 wt% and in step b) the distillation is done at a temperature of 88-112° C and pressure of 85-201 torr.

26. The process for the manufacture of 1,1,1,3-tetrachloropropane of claim 25 wherein in step a) the reactor operates at a temperature of 138° C and at a pressure of 250 psig with a liquid residence time of 11 hours and with a

liquid n-butyronitrile concentration of from 30 wt% and in step b) the distillation is done at a temperature of 104° C and pressure of 154 torr.